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Activation of Molecular Oxygen:
Kinetic Studies of the Oxidation of Hindered Phenols
with Cobalt-Dioxygen Complexes

by
Alan Zombeck, Russell S. Drago,
Barry B. Corden and John H. Gaul

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Contribution from the
School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

ABSTRACT

Mechanistic studies of the oxidation of various substituted
phenols by Co(II) bis(salicylidene-γ-iminopropyl)methylamine,
CoSMDPT are reported. The reaction is first order in (O_2^-),
(substrate) and (Co). A series of experiments are reported to
provide strong support for a mechanistic scheme that involves
reaction of coordinated dioxygen. Coordination of O_2^- to this
cobalt(II) complex enhances the ability of the dioxygen to
abstract hydrogen atoms and to react with phenoxy radicals.
The mechanism provides a rationale for the influence of several
variables on the reaction and suggests steps that were taken to
retard catalyst deactivation.

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INTRODUCTION

Determining the ways dioxygen can be activated by a metal center is important for understanding both biological and commercial systems.[1,2] Though homogeneous catalytic oxidations have been classified in many different fashions,[3,4] they can be separated into four broad categories: (1) free radical autoxidations using simple metal salts; (2) attack by various oxygen-containing nucleophiles on coordinated substrates; (3) oxygen atom transfers from high oxidation state elements; (4) epoxidation of olefins using metal catalysts and alkyl hydroperoxides. Major goals in this field involve controlled, highly selective, oxidations of substrates and demonstration of oxidation capabilities by metal bound O_2.

We became interested in investigating the possibility of catalyzing oxidations with metal-dioxygen adducts. There are many complexes that reversibly bind dioxygen,[5] and the bonding is now understood in terms of the spin-pairing model.[6] Upon coordination of cobalt(II) to dioxygen,[7] partial electron transfer from cobalt to oxygen occurs ranging from $0.1e^-$ to $0.8e^-$ depending on the ligand field surrounding the cobalt.[8] This should provide for variation in the reactivity of the bound O_2. Of the many reported oxidations by O_2, the oxidation of phenols appeared most attractive as a candidate for a process that involves metal coordinated O_2. Numerous reagents and catalysts oxidize phenols and these reactions have been reviewed extensively in the literature.[9-11] Generally, phenols can be oxidized to quinones, coupled products (diphenoquinones), or polymers, depending

on the choice of catalyst or reagent. The oxidation of hindered

phenols by cobalt-salen-dioxygen complexes was first described in

1967 by vanDort and Guerson.[12] High yields of the corresponding

benzoquinone, BQ, were obtained using phenols which were not sub-

stituted in the para position. Several workers[13,14] have

investigated the effect of various reaction conditions on the

product distribution and hypothesize that the monomeric Co-O_2

species produces BQ while the μ-peroxo dimer yields DPQ. While

it is true that reaction conditions will affect the monomer-dimer

equilibrium, Kothari and Tazurma cite evidence to indicate[15]

that the active species leading to both BQ and DPQ is the mono-

nuclear adduct. Cobalt phthalocyanine,[15] CoSMDPT,,[16] Co-acacen,[17]

and cobaloxime derivatives[18] all form dioxygen adducts and have

been found to be active catalysts for this oxidation.

Nishinaga[19] has reported the majority of the recent work

on this subject. He has demonstrated[20] that the monomeric

cobalt-dioxygen complex can abstract a hydrogen atom from a

2,4,6-trisubstituted phenol by showing the simultaneous disappear-

ance of the Co-O_2 EPR signal with the appearance of a phenoxy

radical signal when the oxygen supply is limited. The product of

the reaction of the phenoxy radical with the cobalt(II) complex

and O_2 has been isolated and characterized as the following species.[21]
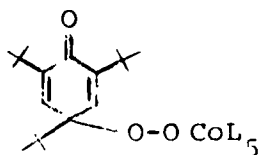
Nishinaga proposes that this product arises from O_2 attack on a

cobalt(III) phenolate complex. Nishinaga's proposed mechanism
is summarized as follows:
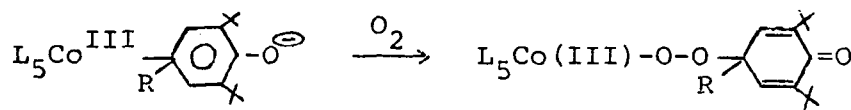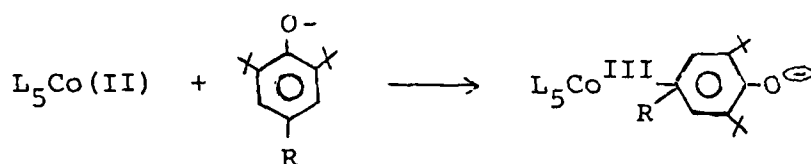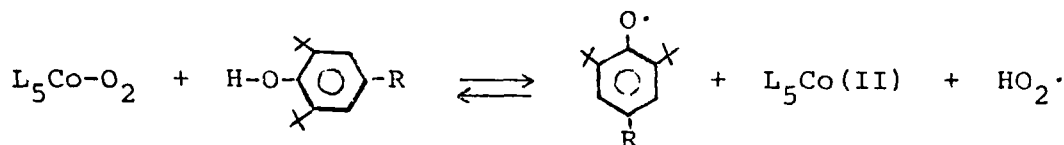
Many unanswered questions remain concerning this important
reaction. To date, the reaction schemes presented are based on
chemical intuition supported by relatively little mechanistic
data. Also, the catalyst undergoes about seventy turnovers and
then becomes relatively ineffective for reasons that are unknown.
Thus, we began a kinetic investigation to provide insight for both
the oxidation of the substrate and the deactivation of the catalyst.
We hoped to gain an understanding of the mechanism of this reaction
to determine if indeed a true dioxygen-activation pathway was
operative, and with this understanding evaluate the potential of
this catalytic system for more difficult oxidations.

EXPERIMENTAL

General

The EPR spectra were collected on a Varian Model E-9 spectrometer equipped with a Hewlett Packard frequency counter. NMR spectra were obtained on a Varian 390 spectrometer. Mass spectra were run by the Mass Spectroscopy Lab at the University of Illinois on a CH-5 instrument. All elemental analyses were performed by the Microanalytical Lab at the University of Illinois.

Materials

The preparation of CoSMDPT, Co(II)bis(salicylidene-γ-iminopropyl)-methylamine, by published procedures[22] was verified by elemental analysis. All phenols were obtained from Aldrich and used without further purification. All solvents were stored over 3A molecular sieves.

Deuterated 2,6-dimethylphenol

A deuterated sample of 2,6-dimethylphenol was prepared by reaction of the starting phenol with methyl-iodide magnesium Grignard reagent, followed by subsequent workup in D_2O. Its mass spectrum showed 70% substitution of OD. The OD stretch is observed at 2520 cm^{-1}.
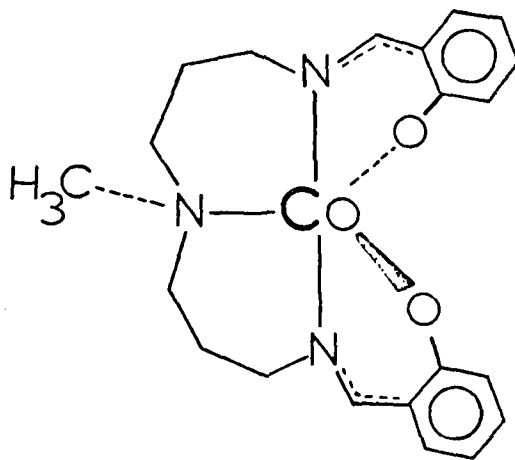
Kinetic studies

The reaction progress was monitored by following the O_2 consumption. The procedure and apparatus for conducting the oxidation at atmospheric pressure has been described previously.[23] Oxidations performed at elevated pressures were conducted in a Parr pressure bottle fitted with a pressure gauge and placed in a temperature controlled oil bath. Typically, a 250 ml pressure bottle was charged with a 50 ml solution of the phenol (concentrations given in text) and magnetic stir bar. The solid cobalt

catalyst would be floated on the solution in a plastic cap. The system was purged several times with O_2 and allowed to equilibrate at the appropriate temperature and pressure (usually 30 min.). Reaction began by stirring the solution and spilling the solid catalyst into the solution. All reactions were stirred at a sufficient rate to ensure mass transfer of dioxygen in the solvent was not rate limiting. The O_2 consumption was found to correlate with product formation. This method gave reproducible results within $\pm$ 1 psi. Reported rates reproducible to within 5% were taken from maximum slopes of the oxygen uptake curves.

Products for the 2,6-di-t-butylphenol oxidation were analyzed by NMR integration of the t-butyl group.[24] After completion of the reaction, $CHCl_3$ was added to insure all products were in solution.

RESULTS

The cobalt complex used in our study was Co(II) bis(salicylidene-γ-iminopropyl)methyl amine, or CoSMDPT. A representation of the complex is shown below;

Kinetic studies

The reaction orders for cobalt, phenol, and O_2 were obtained by independently varying the concentrations of each and monitoring O_2 uptake. All oxidations were conducted in benzene. The O_2 uptake at atmospheric pressure for the reaction at various cobalt concentrations is shown in Figure 1. A plot of $\ln[Co]$ vs. $\ln[d[O_2]/dt]$ yields a straight line with a slope of ´1 (Figure 2) indicating the reaction is first order in [Co] as long as the catalyst is completely dissolved. First order kinetics are observed for phenol concentrations less that 0.09 M (Figure 3). When the ratio of phenol to cobalt becomes greater than 20/1, the rate becomes pseudo zero order in substrate. The reaction was conducted at three different O_2 pressures, while maintaining all other conditions constant. Figure 4 shows the dependence of the rate of the reaction

on the oxygen pressure. The initial rates observed at 60 psi (4.1 atm) and 120 psi (8.2 atm) are approximately 4 and 8 times faster, respectively, than the rate of oxidation at atmospheric pressure, indicating a first order dependence on the O_2 concentration.

When a sample of 2,6-dimethyldeuterophenol was employed as the substrate at 30°C the reaction rate was identical, within experimental error, to the undeuterated sample throughout the duration of the reaction. To ensure that the reaction conditions did not convert some of the deuterated phenol to undeuterated phenol since HOD is produced, a reaction was run with excess D_2O (2 ml, .11 moles) present with the deuterated phenol. The same rate was found for both the deuterated phenol-water and the undeuterated phenol-water experiment, thus indicating an absence of a deuterium isotope effect for this system.

Various phenols were oxidized with CoSMDPT in benzene at 30°C (Table I). In the absence of the steric effects encountered in the 2,4,6-trisubstituted phenols or the 2,6-di-t-butylphenol, the rate increases as the oxidation potential of the phenol decreases. Unsubstituted phenol is oxidized by CoSMDPT in dimethylformamide at higher temperatures and pressures (Table I).

Increasing temperatures up to 50°C results in a faster oxidation of 2,6-dimethylphenol as seen in Figure 5. Temperatures above 70°C have little or no effect on the rate. This behavior indicates the complexity of the reaction mechanism since this increased rate contrasts with the decreased amount of cobalt-dioxygen adduct expected at the higher temperature.[23]

Solvent variation also yields complicated behavior where the rate in chloroform ‹ toluene ≈ benzene > methylene chloride ~ methanol > DMF.

Catalyst Deactivation

In a typical oxidation with excess phenol, O_2 uptake slows substantially by 70 turnovers and declines to almost zero, in roughly the next 20 turnovers. The deactivation of the catalyst (evidenced by the decrease in reaction rate) is accompanied by the precipitation of a brown solid. Chemical analysis of this solid indicates that a considerable increase in the oxygen content of the spent catalyst has occurred compared to CoSMDPT. Typically a 6/1 ratio of O/Co is found in the former.

Studies were initiated to determine the factors that lead to decline in catalytic activity. The change in catalyst lifetime for different conditions is indicated in Table II by the number of turnovers. In these experiments an oxidation was run at 60 psi with a large excess of phenol to cobalt. Uptake is monitored to 30 psi, and then recharged to 60 psi. This cycle is repeated until a noticeable decrease in rate is observed.

The EPR spectrum of a reaction mixture was monitored during the course of an oxidation to determine the correlation of the $Co-O_2$ signal with catalyst deactivation. Aliquots of the reaction mixture taken at various intervals of O_2 uptake show only a $Co-O_2$ signal. Interestingly, this signal remains at relatively the same intensity throughout the reaction; even after the noticeable drop in catalyst activity that occurs at 70 turnovers. This result implies that a product of the oxidation causes a decline in catalytic activity without initially destroying the $Co-O_2$ species. This period is followed by the subsequent oxidation of cobalt(II) to cobalt(III) and the disappearnce of the EPR signal. The major products of the oxidation, BQ and H_2O, do not inhibit the O_2 uptake as shown in Table II. However, acids are found to inhibit cata-
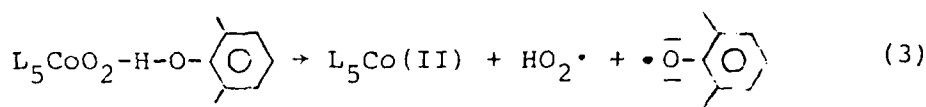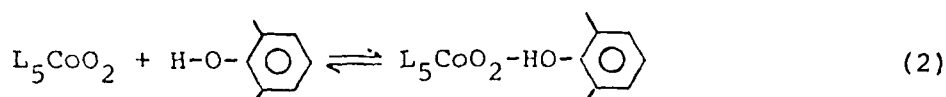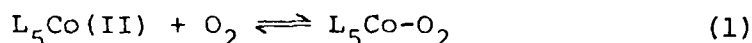
lytic activity. Adding a solution of benzene, saturated with dry HCl, to a solution in the midst of an oxidation reaction results in an immediate end to the O_2 uptake. Inhibition is obtained when solutions of trifluoroethanol or benzoic acid are added. When a weaker acid such as unsubstituted phenol is added to the oxidation reaction, the rate decreases and a large amount of the coupled product DPQ is generated. The EPR of the solution containing TFE and phenol show characteristic Co-O_2 signals, while solutions containing benzoic acid or HCl do not show an EPR signal because rapid oxidation of the cobalt occurs.

Increase turnovers are obtained when the reaction is run in the presence of Na_2CO_3 as seen in Table II. The addition of 2,6-lutidene or polystyrene bound tertiary amine,[27] also increases turnovers with the Na_2CO_3 slurry being most effective. Peroxides formed from decomposition of metal-dioxygen complexes[28] or from HO_2 were suspected as side products that could cause ring cleavage and lead to organic acids that decompose the catalyst. When an aqueous H_2O_2 solution is added to a methanol solution of catalyst, O_2 gas is evolved. When a 30% aqueous H_2O_2 solution is added to a 2,6-dimethylphenol oxidation in methanol solvent the pressure drop is monitored from the initial increased value of pressure from H_2O_2 decomposition. A decline in the number of turnovers (Table II) is reserved.

If H_2O_2 is used as the only oxygen source (the reaction with phenol is run under argon), CoSMDPT catalyzes the decomposition of H_2O_2 to H_2O and O_2 with the simultaneous irreversible oxidation of the cobalt center and no benzoquinone is formed. Thus, the presence of H_2O_2 inhibits the conversion of phenol to quinone.

DISCUSSION

The results of this study clearly indicate that a metal bound dioxygen is an active species in the oxidation of phenol. The following steps are implicated:
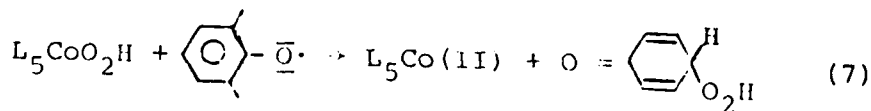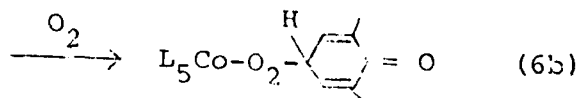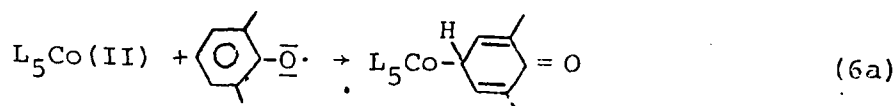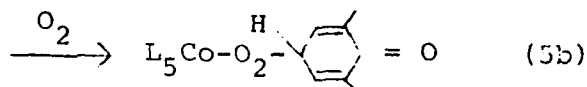
$$L_5Co(II) + O_2 \rightleftharpoons L_5Co-O_2 \qquad (1)$$

$$L_5CoO_2 + H-O-\langle O \rangle \rightleftharpoons L_5CoO_2-HO-\langle O \rangle \qquad (2)$$

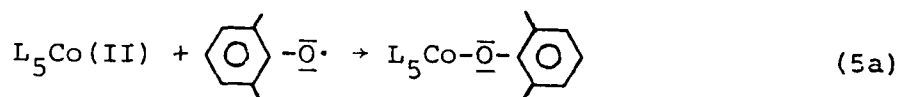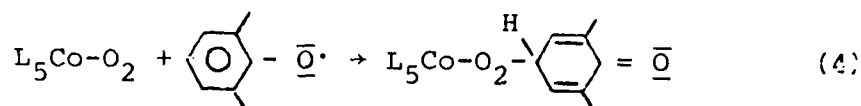$$L_5CoO_2-H-O-\langle O \rangle \rightarrow L_5Co(II) + HO_2\cdot + \cdot\bar{O}-\langle O \rangle \qquad (3)$$

Step 2 is supported by earlier studies in which it is conclusively shown[25] that trifluoroethanol, TFE, undergoes a hydrogen bonding interaction with the terminal oxygen of the cobalt-dioxygen adduct. Although TFE is a stronger acid than 2,6-dimethylphenol,[29] they are close enough in acidity to expect the interaction in equation 2 to occur. Step 3 receives support form the EPR identification of the phenoxy radical formed when 2,4,6-tri-t-butylphenol is oxidized with this catalyst.

There are several paths by which the phenoxy radical can be converted to the quinone. The reaction of the phenoxy radical with free O_2 to form benzoquinone (BQ) is ruled out since the free radical reacts faster with itself in the presence of O_2 to form diphenohydroquinone and subsequently diphenoquinone, DPQ, than it reacts with O_2.[9] The reaction of the phenoxy radical with HO_2 was proposed earlier in a scheme to account for the products of the reaction.[3] This proposal does not seem plausible for the following reason. When HO_2 radicals are intermediates in

autoxidations, large deuterium isotope effects are observed[30]
and this is not the case in our system. Since HO_2 is reported[31]
to decompose at diffusion controlled rates and the slow step in
this reaction occurs subsequent to step 3, <u>vide infra</u>, the fate
of HO_2 is decomposition:

$$2HO_2 \longrightarrow HOOH + O_2$$

The following possible reactions of the phenoxy radical with
cobalt complexes remain to be considered for the next step:

$$L_5Co-O_2 + \langle O \rangle - \underline{O}\cdot \rightarrow L_5Co-O_2-\langle\rangle = \underline{O} \qquad (4)$$

$$L_5Co(II) + \langle O \rangle -\underline{O}\cdot \rightarrow L_5Co-\underline{O}-\langle O \rangle \qquad (5a)$$

$$\xrightarrow{O_2} L_5Co-O_2-\langle\rangle = O \qquad (5b)$$

$$L_5Co(II) + \langle O \rangle -\underline{O}\cdot \rightarrow L_5Co-\langle\rangle = O \qquad (6a)$$

$$\xrightarrow{O_2} L_5Co-O_2-\langle\rangle = O \qquad (6b)$$

$$L_5CoO_2H + \langle O \rangle - \underline{O}\cdot \rightarrow L_5Co(II) + O = \langle\rangle_{O_2H} \qquad (7)$$

The kinetic orders found in this study are consistent with
several of the reactions listed above. Rate expressions can be
derived whose reaction orders are consistent with step 2, or more
likely 3, being rate controlling and 4, 5, 6, or 7 fast. Since
no deuterium isotope effect was observed on the rate of oxidation,
we can eliminate steps 2 or 3 as the rate controlling step.
Mechanisms in which steps 4, 5a, and 6a are rate controlling are
also consistent with the observed rate law if a steady state con-

centration of phenoxy radicals is assumed. Rate controlling steps
for 5b and 6b can be eliminated for they would lead to a second
order dependence on O_2. A rate controlling step 7 is not reasonable
in view of the short lifetime of an L_5CoO_2H species[32] and because
peroxides have not been observed in the reaction medium.[21]
Furthermore, if 7 were a key step, catalysis of the hydroxylation
of 2,4,6-trimethyphenol by CoSMDPT would have been observed.

Several indirect pieces of evidence suggest that in addition
to the hydrogen atom abstraction of the first step, there is in-
volvement of an L_5CoO_2 species in a subsequent reaction with the
phenoxy radical; (Equation 4). The ratio of BQ to DPQ is very
informative in this connection. If this step under consideration
(4, 5a or 6a) is inhibited, the phenoxy radical concentration will
increase, these radicals will couple to form diphenohydroquinone
and be oxidized to diphenoquinone. Data reported earlier[23] on
the catalysis of this oxidation by polystrene bound CoSMDPT suggests
subsequent cobalt involvement (steps 4, 5a or 6a). The BQ/DPQ
ratio is a function of the cobalt loadings in polymer. At high
loadings, where the generated radical has a high probability of
encountering another cobalt-dioxyen center, large ratios of BQ/DPQ
are obtained. At low cobalt concentrations the ratio is reduced
substantially. Encounter of phenoxy radical with a cobalt center
leads to BQ while failure to encounter one leads to DPQ. Several
reagents including solid PbO_2 will generate phenoxy radicals.[33]
When PbO_2 and Co(II) (acetylacetonate)$_2$ (which does not form a
dioxygen adduct under these conditions) catalyzed oxidation of
2,6-dimethylphenol, only diphenoquinone is produced. This result

suggests that the phenoxyl radical needs to encounter a Co-O$_2$ species as shown in step 4 for the production of the quinone. If, as shown in step 5, a cobalt(II) species were sufficient, Co(acac)$_2$ could have fulfilled this requirement.

When competitive hydrogen bonding agents are added to the reaction medium for a 2,6-dimethylphenol, CoSMDPT catalyzed oxidation, the results are readily rationalzed in terms of step 4. When unsubstituted phenol, a slightly stronger acid than 2,6-dimethylphenol, is added to the reaction mixture, the rate of reaction is decreased and the BQ/DPQ ratio is decreased. With the phenol competitively hydrogen bonding to L$_5$CoO$_2$, the phenoxy radical attack on this species is inhibited and DPQ is formed at the expense of BQ.

A reaction in progress can be stopped by adding the stronger acid TFE. Since radicals can be generated by Co(III), vide infra, this suggests a role of other than a radical initiation step for L$_5$CoO$_2$ and we propose equation 4. When stronger acids such as benzoic acid or HCl are added, the reaction stops immediately and this is accompanied by oxidation of cobalt(II) to cobalt(III).

Nishinaga[19] has ruled out the possibility of step 4 being important on the basis of the following experiment: bubbling O$_2$ through a solution of CoSMDPT and 2,4,6-tri-t-butylphenoxy radical produced only the coupled product that resulted from the reaction of the radical with free O$_2$.


(9)
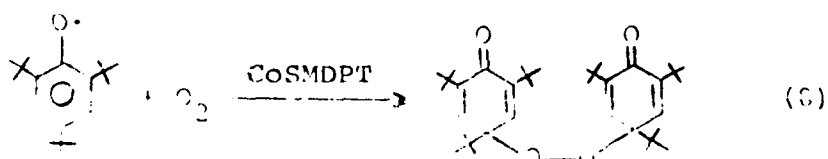
Although experimental details are lacking, there may be two potential drawbacks to this conclusion. First, the concentration of free phenoxy radicals in the oxidation of 2,6-dimethylphenol is extremely low under catalytic reaction conditions (as mentioned above), making the reaction in equation 8 much less probable. Second, the concentration of Co-O$_2$ in the above experiment is expected to be lower than that in the phenol oxidation because it has been shown that the equilibrium in step 1 is enhanced[25] by the addition of hydrogen bonding substrates via step 2. Thus, the concentration of L$_5$CoO$_2$ in a solution of phenoxy radicals is considerably less than what is found in a typical phenol oxidation. Instead of step 4, steps 6a and 6b are proposed [19] as the mechanism for quinone formation. Formation of a Co-C bond is followed by subsequent O$_2$ insertion to produce the cobalt-peroxy-quinone compound. We prepared the cobalt-peroxy-quinone complex of 2,4,6-tri-t-butylphenol reported by Nishinaga[20] and observed a very interesting phenomena in the EPR. If a toluene/CH$_2$Cl$_2$ glass of this complex is prepared, the EPR specturm in Figure 6 is observed. It displays overlapping spectra of the free phenoxy radical and Co-O$_2$ signal. Thus, the phenoxy radical plus L$_5$CoO$_2$ are in equilibrium with the cobalt-peroxo-quinone. This is most readily visualized as occurring via the reverse reaction of step 4 and would support the direct pairing of radicals in the oxidation as opposed to an unprecedented reversible O$_2$ insertion (the reverse of step 6).

The remaining problem involves the step for converting L$_5$Co-O$_2$- ⬡ =O to the quinone and regenerating the catalyst. There is no direct information bearing on this problem. By

analogy with the decomposition of an organic hydroperoxide, we
propose the following reaction for quinone formation:

$$L_5CoO_2 - \text{[phenol ring]} =O \quad \rightarrow \quad L_5Co(III)OH + \quad O=\text{[quinone ring]}=O \qquad (9)$$
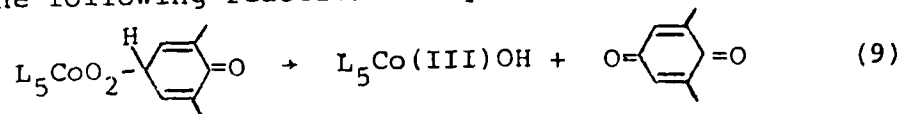
The Co(II) species could be regenerated by phenol oxidation as
follows:

$$L_5Co(III)OH + HO-\text{[ring]} \quad \rightarrow \quad L_5Co(II) + H_2O + \cdot\overline{O}-\text{[ring]} \qquad (10)$$
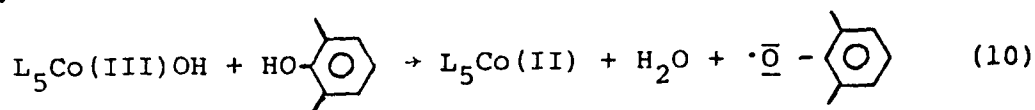
The fate of the HO_2 generated in step 3 is worth considering
further. The rate of self reaction of HO_2 approaches the diffusion
controlled limit in nonpolar solvents.[31] It could be converted
to hydrogen peroxide by hydrogen atom abstraction from phenol and
the peroxide can be decomposed into water and O_2 by the cobalt(II)
complex. Minor side reactions involving small amounts of HO_2
radical or hydrogen peroxide are probably implicated in the cata-
lyst degradation reaction. Carboxylic acids formed from ring
opening reactions would block step 2 above and stop oxidation

by inhibiting formation of the phenoxy radical. The observation
of a cobalt-O_2 EPR of undiminished intensity in the deactivated
catalyst is consistent with such a hydrogen bonded carboxylic acid-
cobalt dioxygen adduct. Carboxylic acids can arise by attack of
HO_2 on quinones or via Baeyer-Villiger type attacks of peroxides
on ketones. Experiments designed to test this speculation led to
a very significant improvement in catalyst lifetime. Addition of
base to the reaction mixture greatly extended the number of turn-
overs by the catalyst. The most basic material, Na_2CO_3, was
most effective. The role of a base is not well established, how-
ever, since the pK_a of HO_2 is 4.9 it should be converted into a

superoxide anion by the addition of these bases.[34] Thus we
propose that equations 1, 2, 3, 4, 9 and 10 constitute the reac-
tion both for the formation of quinone, and the regeneration of
the catalyst.

The metal plays two important roles in the catalysis of
this oxidation: (1) coordination activates the O_2 molecule and en-
hances its ability to abstract hydrogen atoms; (2) coordination
enhances the activity of the O_2 molecule in a free radical reaction
with organic molecules. There are many aspects of the mechanism
of this oxidation reaction that remain speculative. We have,
however, presented results that rule out many of the possible
paths. Our proposed mechanism is summarized in Figure 7. The
extension of a reaction pathway for a given system to other sub-
strates is always a dangerous practice and this lack of generality is
one of the shortcomings of kinetic investigations. In this study,
we have been able to provide a scheme for the oxidation of 2,6-
dimethylphenol that is consistent with the known reactivity of
this and analogous substrates. We have also been able to demon-
strate that coordination of dioxygen to a metal enhances the rate
at which it undergoes the spin-pairing reaction with organic free
radicals.

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TABLE I

PHENOL	$(OP)_o$ [26]	ΔP (psi)	Time (min)	Total turnovers[a]	Turnovers per hour
1. 2,4,6 TRIMETHYL[c]	.67	26	1190	20.4	1.6
2. 2,6 di-t-Butyl	.68	33	310	24.9	4.8
3. 2,3,5,6 tetramethyl	.71	40	97	27.7	13.6
4. 2,6 diisopropyl	.74	40	188	30.1	15.4
5. 2,6 dimethyl	.76	43	131	32.3	14.8
6. 2,5 di-t-Butyl	.83	12	1415	9.1	.4
7. 3,5 dimethyl	.86	15	930	11.3	.4
8. phenol[d]	.92	18	1060	14.1	.8
9. 2,6 dichloro	——	0	300	0	0

All oxidations were .49M in phenol and .0146M in CoSMDPT, 50ml of benzene used as solvent, temperature = 30°C, initial pressure of O_2 = 60 psi.

a Total turnovers = moles O_2 consumed/mole Co before rate of O_2 uptake begins to decline.

b Turnovers per hour = mole O_2 consumed/mole Co·hr, based on initial rates.

c DMF used as solvent.

d DMF used as solvent, temperature = 75°C, initial O_2 pressure = 120 psi.

TABLE II

Oxidation of 2,6 Dimethylphenol; Determination of

Catalytic Activity with Various Additives

	mmoles of Additives	ΔP (psi)	Time (hrs)	Total Turnovers
No Additive	——	68	20.5	76
2,6 dimethylbenzoquinone	10.5	83	17.5	93
2,6 dimethylbenzoquinone	33.0	86	18	96
2,6 dimethylbenzoquinone + H_2O	33.0	82	18	92
Na_2CO_3 slurry[a]	36.7	56	20.5	249
Fe(acac)$_2$Cl	36.7	70	20.5	78
MeOH (solvent)[b]	——	48	20.5	200
H_2O_2 in MeOH[b]	17.6	51	20.5	46
H_2O_2 in MeOH plus 2,6 dimethylbenzoquinone	17.6	21	20.5	24

All oxidations were conducted in 50 ml of benzene, unless stated otherwise, with 7.37×10^{-2} moles of 2,6 dimethylphenol, and 4.88×10^{-4} moles CoSMDPT, temperature = 30°C. [a]Small amount of a crown ether added as well to act as a phase transfer catalyst, but was later found not to be necessary. [b]1.24×10^{-4} moles CoSMDPT to accomodate the large number of turnovers at comparable phenol concentrations.

FIGURE CAPTIONS

Figure 1. Oxygen uptake curves for oxidation of 2,6-dimethylphenol
$(4.0 \times 10^{-2} \underline{M})$, with CoSMDPT. Cobalt concentrations are (1)
$4.014 \times 10^{-2} \underline{M}$, (2) $2.996 \times 10^{-2} \underline{M}$, (3) $2.202 \times 10^{-2} \underline{M}$, (4)
$2.00 \times 10^{-2} \underline{M}$, (5) $1.252 \times 10^{-2} \underline{M}$, (6) $1.014 \times 10^{-2} \underline{M}$,
(7) $0.620 \times 10^{-2} \underline{M}$.

Figure 2. Plot of $\ln[dO_2/dt]$ _versus_ $\ln[Co]$ (from Figure 1). Slope
indicates reaction order for cobalt = 1.

Figure 3. First order kinetic plot for oxidation of 2,6 dimethyl-
phenol with CoSMDPT $(4 \times 10^{-3} \underline{M}$ in Co) in 25 ml of benzene.

Figure 4. Oxidation of 2,6 dimethylphenol $(.494 \underline{M})$ with CoSMDPT
$(.0146 \underline{M})$ in 50 ml of benzene. Temperature = 30°C, O initial
pressure 120 psi, ◐ initial pressure 60 psi.

Figure 5. Oxidation of 2,6 dimethylphenol at various temperatures
$[Co] = .0146 \underline{M}$ [phenol] = $.49 \underline{M}$ in 50 ml of toluene.

Figure 6. CH_2Cl_2/toluene frozen glass EPR (x-band) spectrum of
$Co-O_2$ and phenoxyl radical.

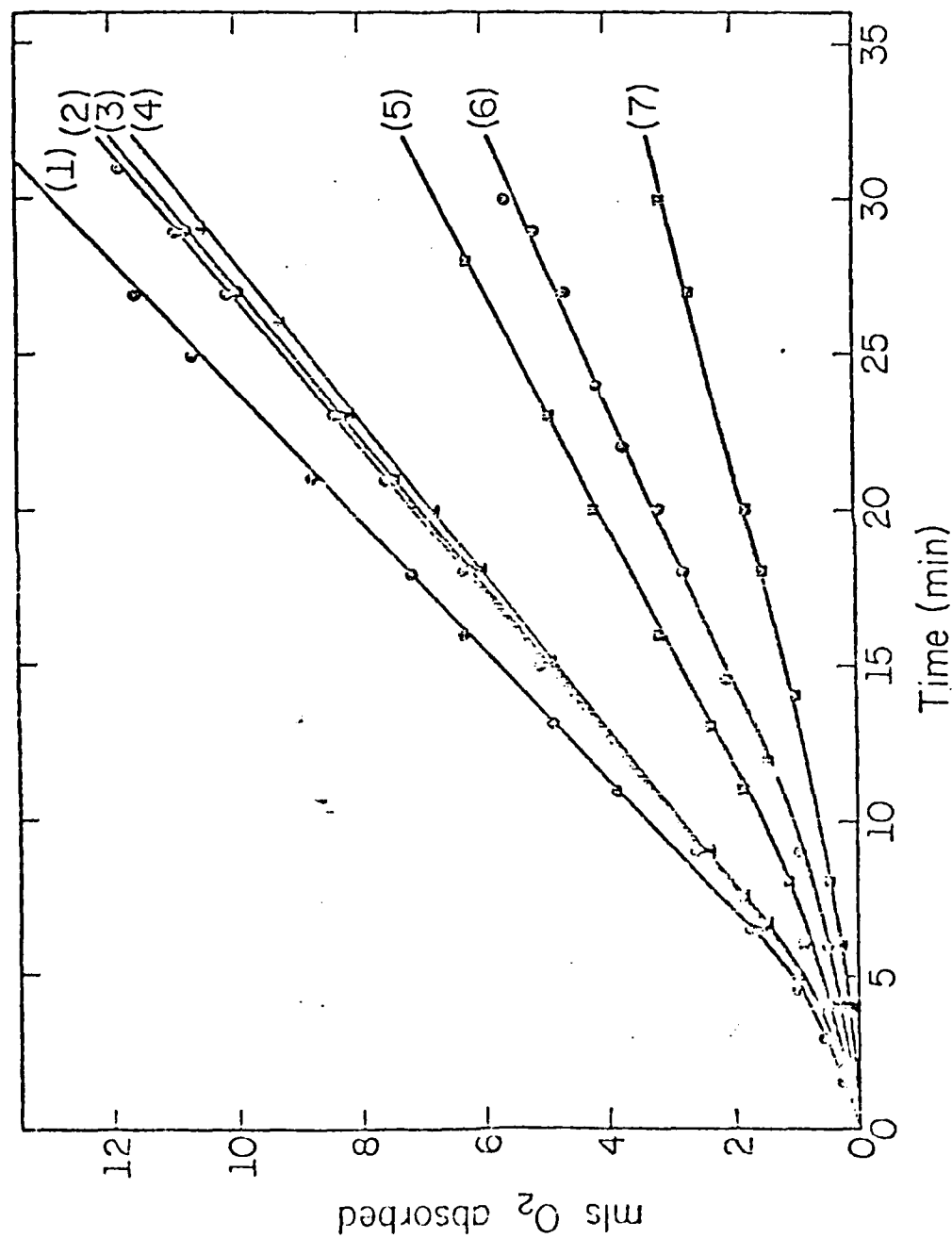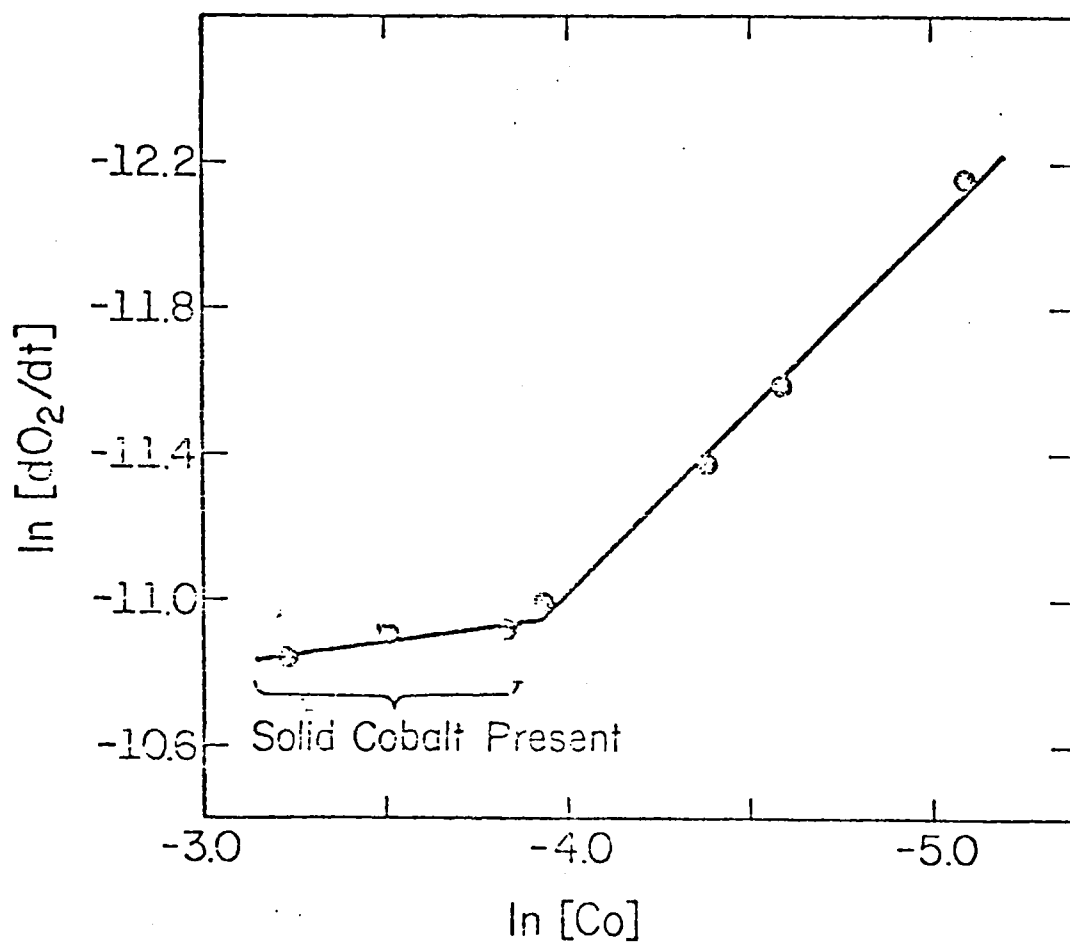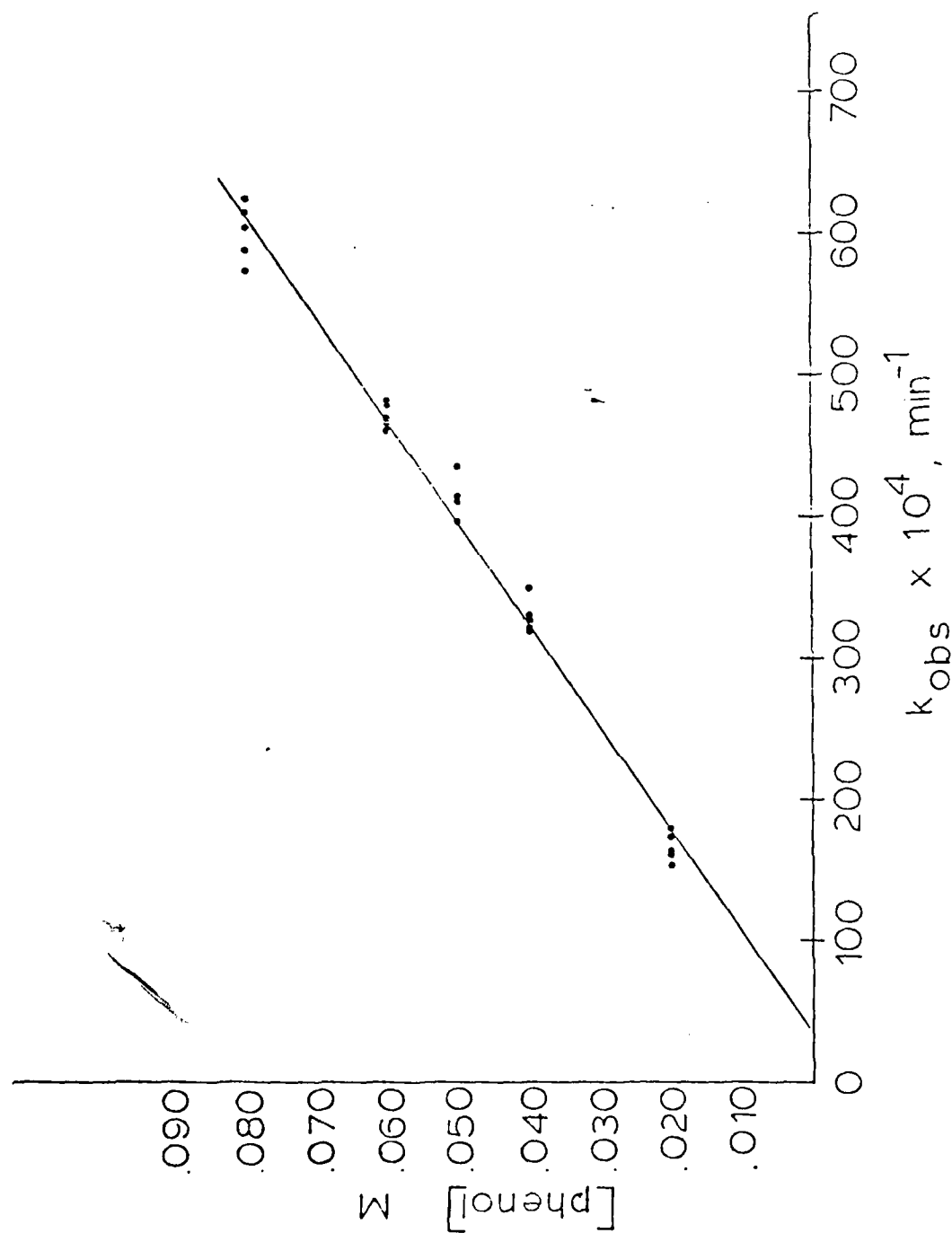Figure 7. Proposed mechanism for the oxidation of 2,6 dimethylphenol
by CoSMDPT.

Figure 1. Oxygen uptake curves for oxidation of 2,6-dimethylphenol (4.0×10^{-2} $\underline{M}$), with CoSMDPT. Cobalt concentrations are (1) 4.014×10^{-2} $\underline{M}$, (2) 2.996×10^{-2} $\underline{M}$, (3) 2.202×10^{-2} $\underline{M}$, (4) 2.00×10^{-2} $\underline{M}$, (5) 1.252×10^{-2} $\underline{M}$, (6) 1.014×10^{-2} $\underline{M}$, (7) 0.620×10^{-2} $\underline{M}$.

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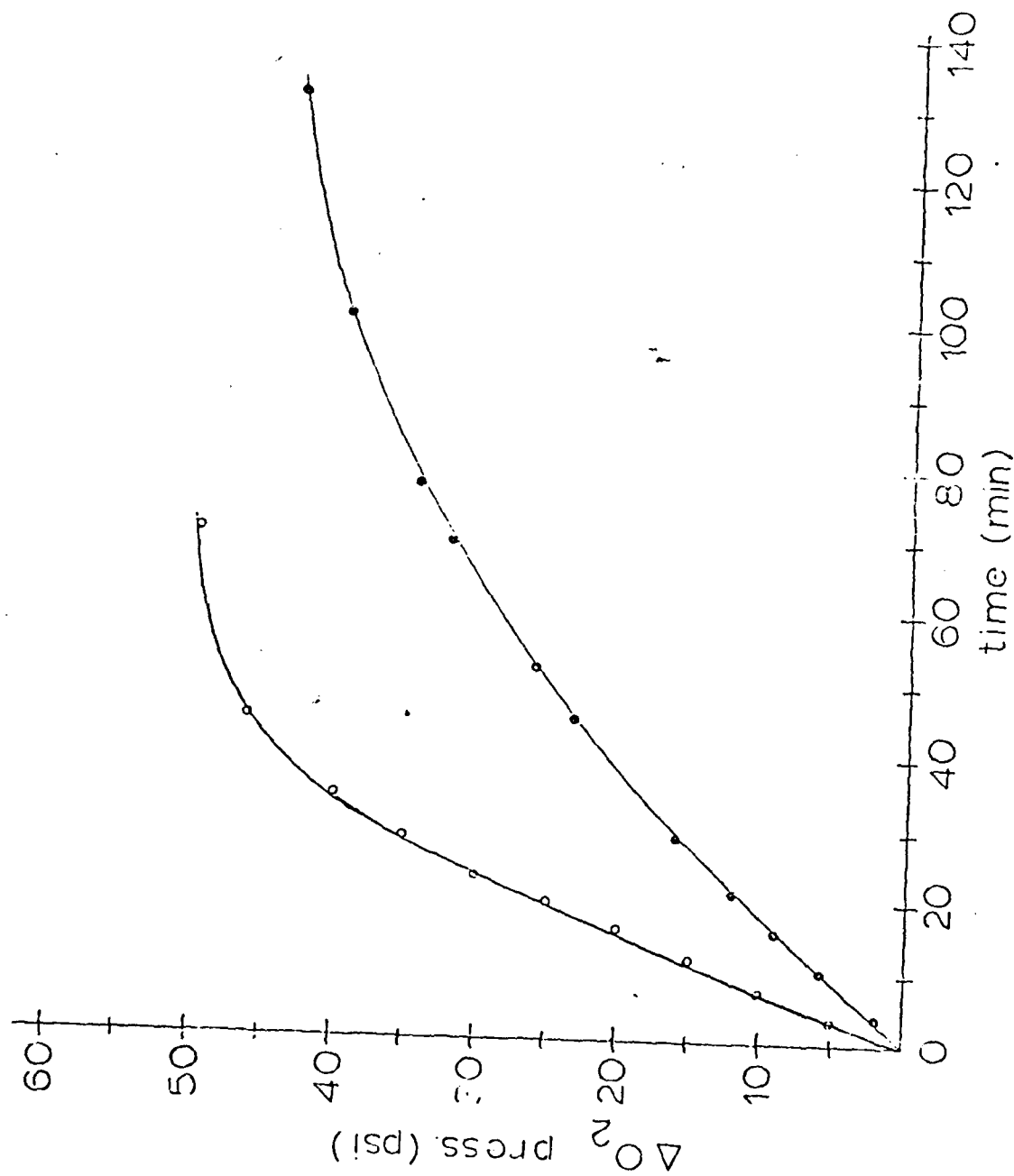
Figure 4. Oxidation of 2,6 dimethylphenol (.494 M) with CoSMDPT (.0146 M) in 50 ml of benzene. Temperature = 30°C, O initial pressure 120 psi, ● initial pressure 60 psi.
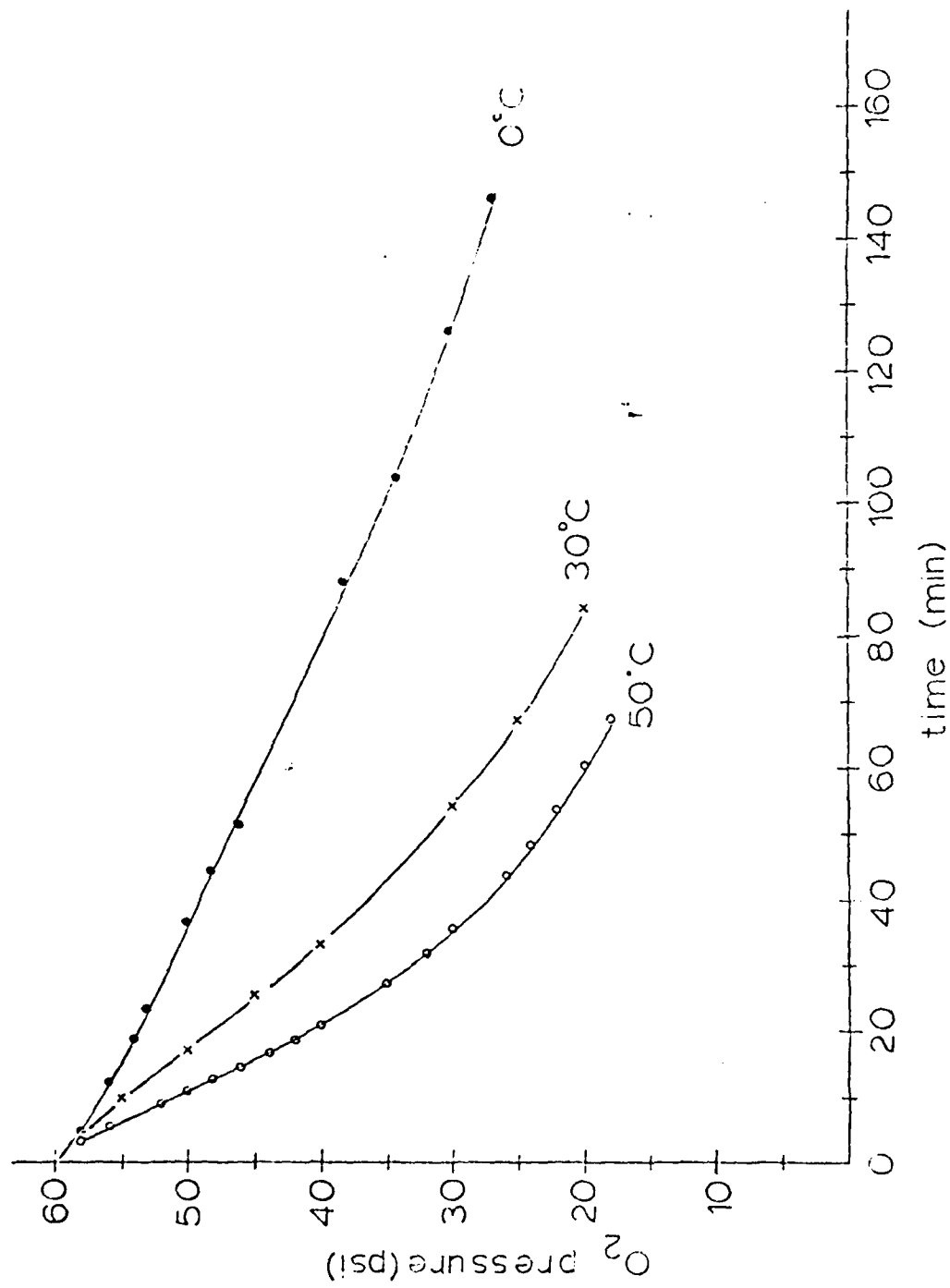
Figure 5. Oxidation of 2,6 dimethylphenol at various temperatures [Co] = .0146 M [phenol] = .49 M in 50 ml of toluene.
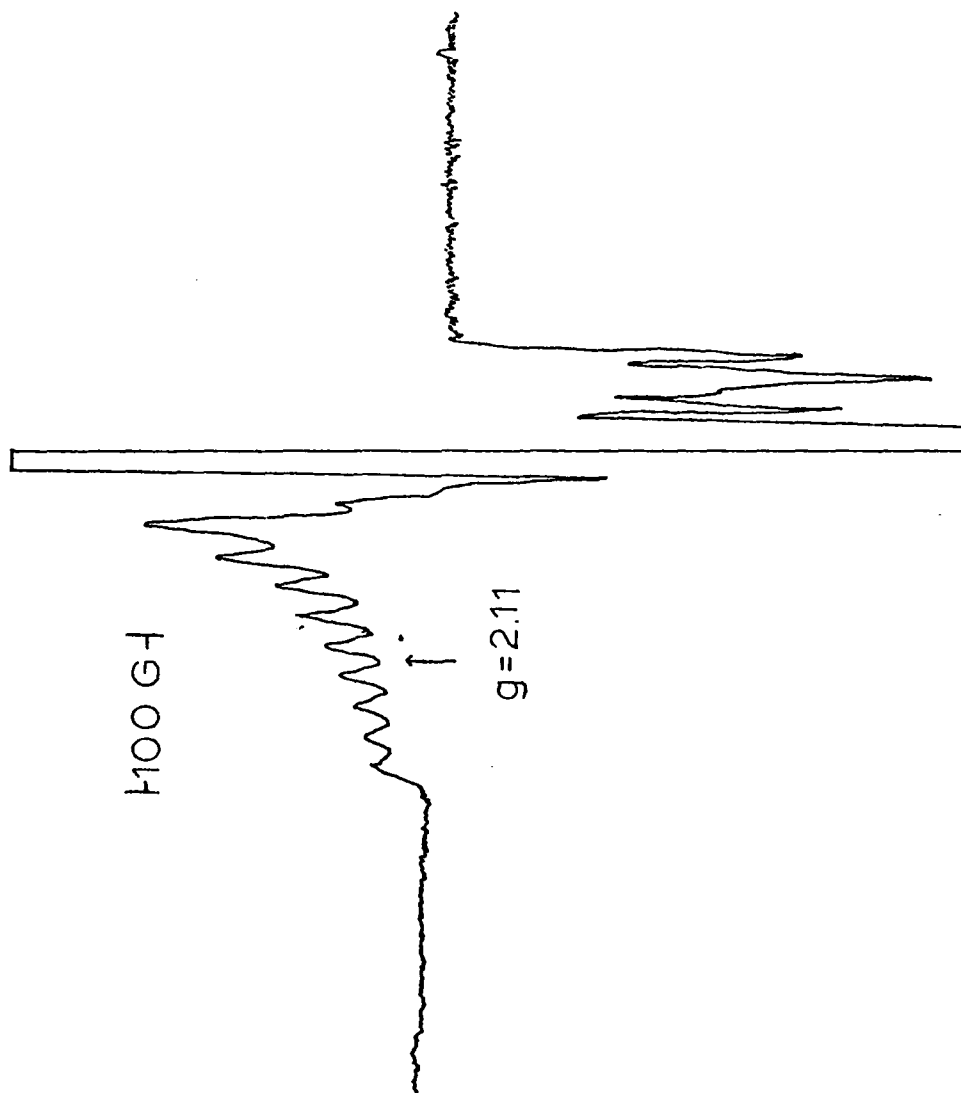
H100 G⊣

g=2.11

Fig⹀e 6. CH$_2$Cl$_2$/toluene frozen glass EPR (x-band) spectrum of Co-O$_2$ and phenoxyl radical.
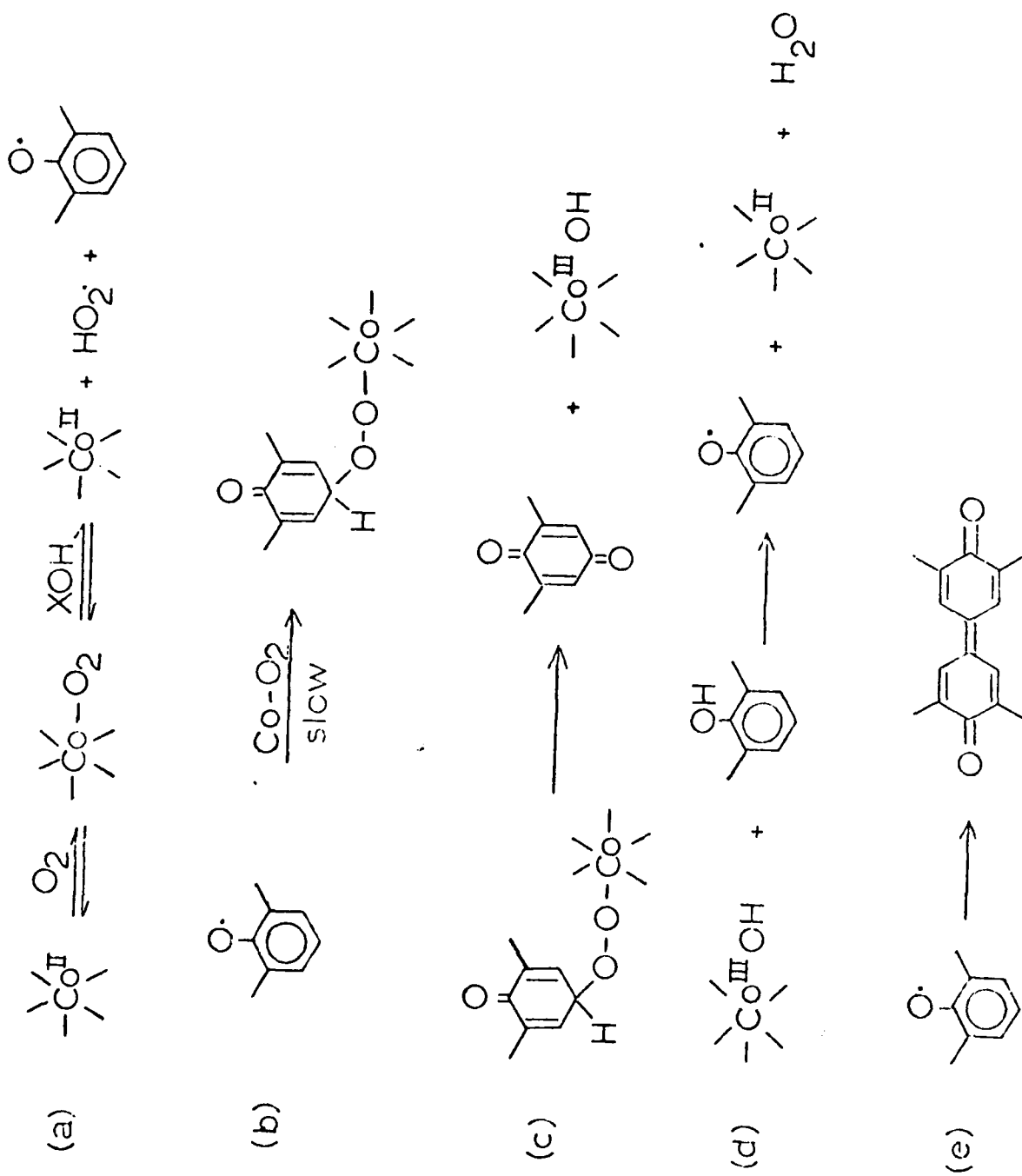
Figure 7. Proposed mechanism for the oxidation of 2,6-dimethylphenol by CoSMDPT